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Tandem Synthesis of N-Alkylated Amides from Aldoximes and Alcohols by Using a Ru/Ir Dual-Catalyst System

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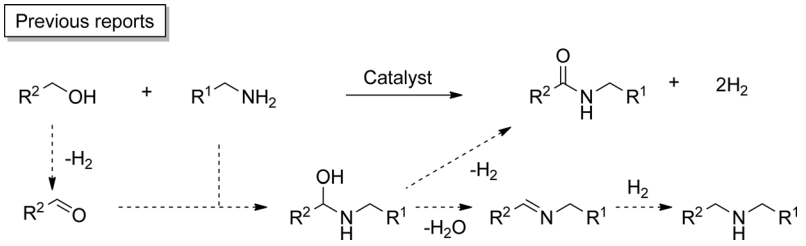
N-alkylated amides constitute an important class of nitrogen-containing compounds that are widely utilized in fine chemicals, natural products, pharmaceuticals, peptides, and polymers.[1] Traditionally, N-alkylated amides are synthesized by the coupling of carboxylic acids or their derivatives (e.g., acid chlorides, anhydrides, and esters) with N-alkylated amines.[2] In addition, the Beckmann rearrangement,[3] the Schmidt rearrangement,[4] Staudinger ligation,[5] the aminocarbonylation of aryl halides,[6] and the oxidative amidation of aldehydes[7] have been employed for the preparation of N-alkylated amides. However, these procedures typically require stoichiometric amounts of hazardous and/or expensive reagents and they suffer from the generation of at least stoichiometric amounts of harmful waste byproducts.



Scheme 1. Strategy for the synthesis of N-alkylated amides from amines and alcohols.

In 2007, Milstein and co-workers reported a strategy for the synthesis of N-alkylated amides from amines and primary alcohols catalyzed by a PNN-type ruthenium complex.[8] Presumably, the alcohols are first dehydrogenated to form their corresponding aldehydes, which are condensed with amines to afford hemiaminal intermediates; finally, the hemiaminals are hydrogenated to give N-alkylated amides (Scheme 1). This procedure is attractive because alcohols are readily accessible and inexpensive starting materials and because hydrogen gas is liberated as a byproduct. Following this pioneering work, several groups have developed this transformation by using other transition-metal catalysts, such as the combination of a N-heterocyclic carbene (NHC) precursor with $[\{Ru(cod)Cl\}_2]$,[9] $[\{Ru(p\text{-cymene})Cl_2\}_2]$, $[[Ru(benzene)Cl_2\}_2]$,[10] or $[RuH_2(PPh_3)_4]$ systems,[11] N-heterocyclic-carbene-based ruthenium complexes,[12] ruthenium-diphosphine-diamine complexes,[13] and γ-alumina-supported silver clusters.[14] Despite these significant advances, controlling the last step of the reaction mechanism is still extremely challenging because the resulting hemiaminal intermediates may also eliminate water to form imines, which can undergo hydrogenation with the liberated hydrogen gas to generate amines (Scheme 1). From both synthetic and environmental points of view, the development of an alternative control strategy for the preparation of N-alkylated amides from alcohols would be of significant importance.

In recent years, tandem catalysis, which is capable of promoting multiple mechanistically distinct reactions in a single reactor, has becoming increasingly important as an alternative to traditional multistep synthetic procedures, owing to it minimizing the use of chemicals, energy, and waste production.[15] Transition-metal complexes, such as rhodium,[16] ruthenium,[17] and iridium complexes,[18] have been utilized as efficient catalysts for the rearrangement of aldoximes into amides. On the other hand, the N-alkylation of various amines with alcohols as alkylating agents was developed, based on "hydrogen autotransfer" (or "hydrogen-borrowing") processes,[19] by using iridium,[20] ruthenium,[21] or other transition-metal catalysts.[22] Very recently, we reported transition-metal-catalyzed direct N-alkylation reactions with alcohols for the preparation of 2-(*N*-alkylamino)azoles,[23a–d] 2-(*N*-alkylamino)quinazolines,[23e] *N*,*N*′-alkylarylureas, and *N*,*N*′-dialkylureas,[23f] thus exhibiting the potential of alcohols (rather than alkyl halides) as electrophiles in regioselective reactions. As part of our continuing interest in exploring C–N bond-forming reactions, herein, we report the first example of the direct synthesis of N-alkylated amides from aldoximes and alcohols through tandem rearrangement/N-alkylation reactions. The proposed mechanism is outlined in Scheme 2. In the presence of a catalyst(s), aldoximes first rearrange into amides, followed by alkylation of the resulting amides with alcohols to afford N-alkylated amides.

Initially, a range of commercially available ruthenium, rhodium, and iridium complexes, including $[\{Ru(p\text{-cymene})Cl_2\}_2]$, $[(Cp^*RhCl_2)_2]$ (Cp^* = pentamethylcyclopentadienyl), $[\{Rh(cod)Cl\}_2]$ (cod = 1,5-cyclooctadienyl), $[(Cp^*IrCl_2)_2]$, and $[\{Ir(cod)Cl\}_2]$ were assayed for their ability to catalyze the rearrangement of benzaldoxime (**1a**) into benzamide (**3a**) and the N-alkylation of compound **3a** with benzyl alcohol (**2a**) to afford N-alkylated compound **4aa**. As outlined in Equations (1) and (2), various complexes exhibited catalytic activity for both the rearrangement and N-alkylation reactions, although the

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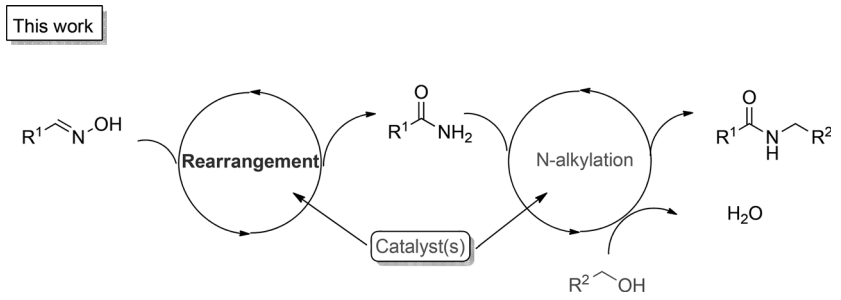
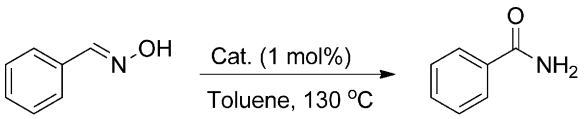


Scheme 2. Strategy for the synthesis of N-alkylated amides from aldoximes and alcohols.

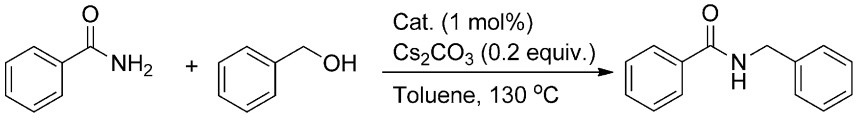
yields varied significantly with the catalyst species. Among them, [{Ru(*p*-cymene)Cl_2}$_2$] (1 mol%) was the most effective catalyst for the rearrangement of compound **1a** and the product (**3a**) was obtained in 96% yield after 3 h [Eq. (1)]. In the presence of [(Cp*$IrCl_2$)$_2$] (1 mol%) and Cs_2CO_3 (0.2 equiv), the reaction of compound **3a** with compound **2a** was performed at 130 °C for 12 h to afford the N-alkylated product (**4aa**) in the highest yield (95% yield) [Eq. (2)].[24] Furthermore, [{Ru(*p*-cymene)Cl_2}$_2$], [(Cp*$IrCl_2$)$_2$], and [{Ru(*p*-cymene)Cl_2}$_2$]/[(Cp*$IrCl_2$)$_2$] were chosen as the catalyst systems for the tandem rearrangement/N-alkylation reactions. In the presence of the [{Ru(*p*-cymene)Cl_2}$_2$] (0.5 mol%)/[(Cp*$IrCl_2$)$_2$] (0.5 mol%) catalytic system, the reaction of compound **1a** proceeded at 130 °C for 3 h to give intermediate **3a** with almost-quantitative conversion, which was further converted into compound **4aa** in 90% yield if compound **2a** (1.2 equiv) and Cs_2CO_3 (0.2 equiv) were added into the reactor for 12 h. If [{Ru(*p*-cymene)Cl_2}$_2$] (1.0 mol%) or [(Cp*$IrCl_2$)$_2$] (1.0 mol%) were used as single catalysts, the product (**4aa**) was obtained in only moderate yields [Eq. (3)].[25]

Having established the Ru/Ir dual-catalyst system, the reactions of compound **1a** with a variety of alcohols (**2**) were examined and the results are summarized in Table 1. The reactions of compound **1a** with benzylic alcohols that contained an electron-donating group, such as methyl (**2b**), isopropyl (**2c**), and methoxy groups (**2d**) afforded the desired products (**4ab**–**4ad**) in 81%–87% yield (Table 1, entries 1–3). Similarly, the reactions with benzylic alcohols that contained one or two halogen atoms (**2e**–**2h**) gave the corresponding products (**4ae**–**4ah**) in high yields (Table 1, entries 4–7). Moreover, a benzylic alcohol that contained a strongly electron-withdrawing trifluoromethoxy group (**2i**) was converted into the desired product (**4ai**) in 83% yield (Table 1, entry 8). Furthermore, the reactions with 1-naphthalenemethanol (**2j**) and 2-naphthalenemethanol (**2k**) affording their corresponding products (**4aj** and **4ak**) in 82% and 86% yield, respectively (Table 1, entries 9 and 10). If aliphatic alcohols, such as 1-butanol (**2l**), 3-methylbutan-1-ol (**2m**), and cyclohexylmethanol (**2n**) were utilized as reagents under solvent-free conditions, the desired products (**4al**–**4an**) were successfully obtained, although higher temperatures and a stronger base were required (Table 1, entries 11–13). In the case of secondary alcohols with high steric hindrance, such as cyclohexanol and cyclopentanol, none of the corresponding N-alkylated products were obtained.



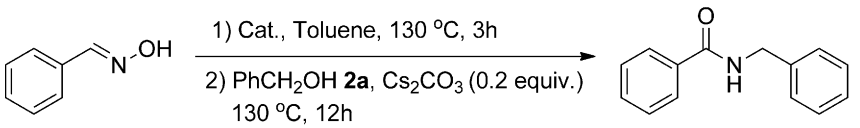
1a **3a** (1)

Cat. = **[Ru(*p*-cymene)Cl_2]$_2$, 96% yield, 3h**
[Cp*$RhCl_2$]$_2$, 15% yield, 3h
[Rh(cod)Cl]$_2$, 87% yield, 3h
[Cp*$IrCl_2$]$_2$, 85% yield, 3h
[Ir(cod)Cl]$_2$, 82% yield, 3h



3a **2a** (1.2 equiv.) **4aa** (2)

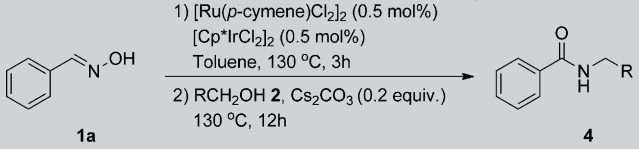
Cat. = [Ru(*p*-cymene)Cl_2]$_2$, 82% yield, 12h
[Cp*$RhCl_2$]$_2$, 26% yield, 12h
[Rh(cod)Cl]$_2$, 20% yield, 12h
[Cp*$IrCl_2$]$_2$, 95% yield, 12h
[Ir(cod)Cl]$_2$, 79% yield, 12h

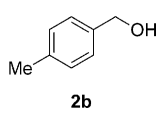
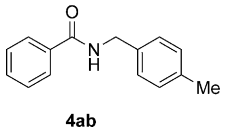
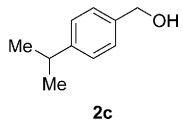
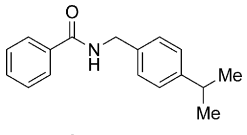
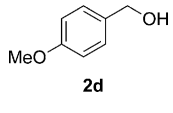
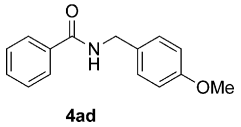
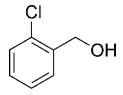
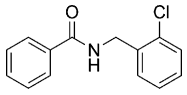
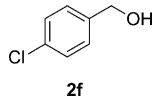
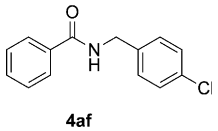
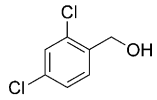
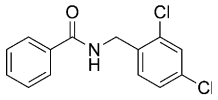
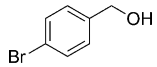
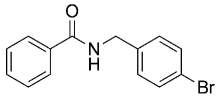
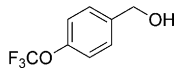
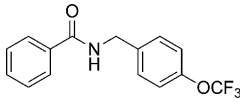
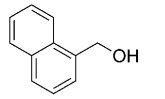
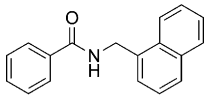
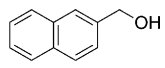
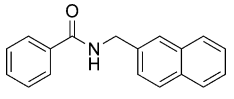
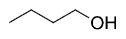
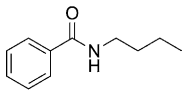
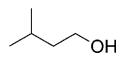
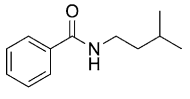
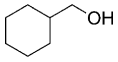
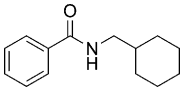


1a **4aa** (3)

Cat. = [Ru(*p*-cymene)Cl_2]$_2$ (1 mol%), 75% yield
[Cp*$IrCl_2$]$_2$, (1 mol%), 77% yield
[Ru(*p*-cymene)Cl_2]$_2$ (0.5 mol%)/[Cp*$IrCl_2$]$_2$ (0.5 mol%), 90% yield

Table 1. Reactions of benzaldoxime (**1a**) with a variety of alcohols (**2**).[a]

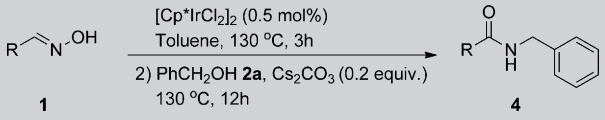


Entry	Alcohol	Product	Yield [%][b]
1	 **2b**	 **4ab**	87
2	 **2c**	 **4ac**	81
3	 **2d**	 **4ad**	83
4	 **2e**	 **4ae**	89
5	 **2f**	 **4af**	92
6	 **2g**	 **4ag**	88
7	 **2h**	 **4ah**	91
8	 **2i**	 **4ai**	83
9	 **2j**	 **4aj**	82
10	 **2k**	 **4ak**	86
11	 **2l**	 **4al**	81[c]
12	 **2m**	 **4am**	78[c]
13	 **2n**	 **4an**	85[c]

[a] Reactions conditions: Compound **1a** (1 mmol), [{Ru(*p*-cymene)Cl_2}$_2$] (0.5 mol%), [(Cp^*IrCl_2)$_2$] (0.5 mol%), toluene (1 mL), 130 °C, 3 h; then, compound **2** (1.2 mmol) and Cs_2CO_3 (0.2 equiv) were added into the reactor, 130 °C, 12 h. [b] Yield of isolated product. [c] Reactions conditions: compound **1a** (1 mmol), compound **2** (4 equiv), [{Ru(*p*-cymene)Cl_2}$_2$] (0.5 mol%), [(Cp^*IrCl_2)$_2$] (0.5 mol%), solvent-free, 130 °C, 3 h; then, KO*t*Bu (0.4 equiv) was added into the reactor, 150 °C, 12 h.

To further expand the scope of this reaction, the reactions of a series of aldoximes (**1**) with compound **2a** were investigated. As shown in Table 2, the reactions of benzaldoximes that con-

Table 2. Reactions of a series of aldoximes (**1**) with benzyl alcohol (**2a**).[a]



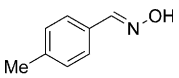
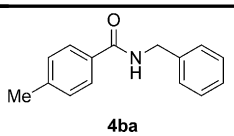
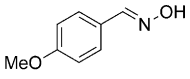
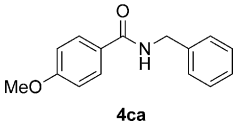
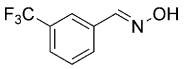
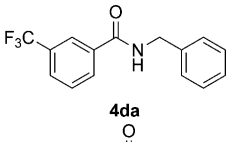
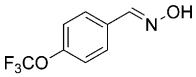
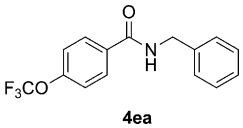
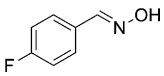
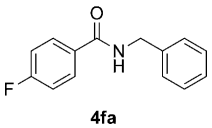
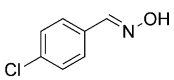
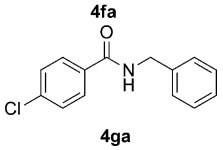
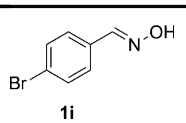
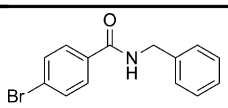
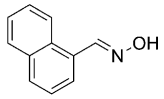
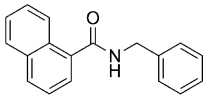
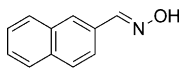
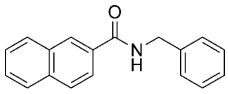
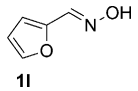
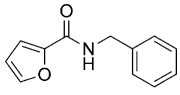
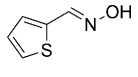
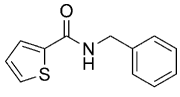
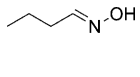
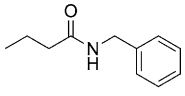
Entry	Aldoxime	Product	Yield [%][b]
1	 **1b**	 **4ba**	88
2	 **1c**	 **4ca**	85
3	 **1d**	 **4da**	82
4	 **1e**	 **4ea**	84
5	 **1f**	 **4fa**	86
6	 **1g**	 **4ga**	93
7	**1h**	**4ha**	88

Table 2. (Continued)

Entry	Aldoxime	Product	Yield [%][b]
8	 **1i**	 **4ia**	90
9	 **1j**	 **4ja**	81[c]
10	 **1k**	 **4ka**	85[c]
11	 **1l**	 **4la**	82
12	 **1m**	 **4ma**	87
13	 **1n**	 **4na**	77[d]

[a] Reactions conditions: Compound **1** (1 mmol), [{Ru(*p*-cymene)Cl_2}$_2$] (0.5 mol%), [(Cp*$IrCl_2$)$_2$] (0.5 mol%), toluene (1 mL), 130 °C, 3 h; then, compound **2a** (1.2 mmol) and Cs_2CO_3 (0.2 equiv) were added into the reactor, 130 °C, 12 h. [b] Yield of isolated product. [c] KO*t*Bu was used instead of Cs_2CO_3. [d] KO*t*Bu (0.4 equiv) was used instead of Cs_2CO_3, 150 °C.

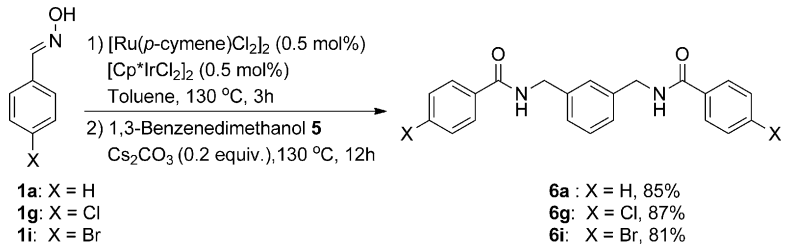
tained an electron-donating substituent, such as methyl (**1b**) and methoxy groups (**1c**), gave the corresponding products (**4ba** and **4ca**) in 88% and 85% yield, respectively (Table 2, entries 1 and 2). The transformation of benzaldoximes that contained a strongly electron-withdrawing substituent, such as trifluoromethyl (**1d**) and trifluoromethoxy groups (**1e**), afforded the desired products (**4da** and **4ea**) in 82% and 84% yield, respectively (Table 2, entries 3 and 4). Furthermore, high catalytic activities were observed in the reactions of benzaldoximes that contained one or two halogen atoms (**1f**–**1i**) and the corresponding products (**4fa**–**4ia**) were obtained in 86–93% yield (Table 2, entries 5–8). The transformations of 1-naphthaldoxime (**1j**) and 2-naphthaldoxime (**1k**) afforded the desired products (**4ja** and **4ka**) in 81% and 85% yield, respectively (Table 2, entries 9 and 10). Moreover, if heteroaromatic aldoximes **1l** and **1m** were employed as substrates, N-alkylated products **4la**–**4ma** were also obtained in high yields (Table 2, entries 11 and 12). The reaction was also applied to aliphatic aldoxime **1n**, thus affording the corresponding product (**4na**) in 77% yield (Table 2, entry 13).

Next, the reactions of various aldoximes with a diol were investigated. Thus, the reactions of benzaldoxime derivatives **1a**, **1g**, and **1i** with 1,3-benzenedimethanol (**5**) afforded the corresponding N,N′-dialkylated products (**6a**, **6g**, and **6i**) in 81–87% yield (Scheme 3).

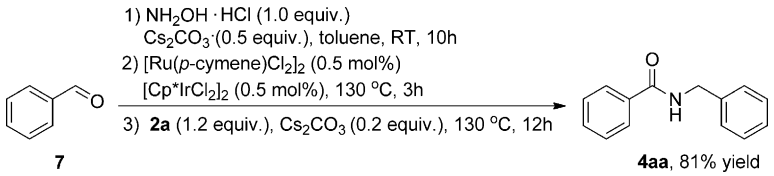
Finally, the one-pot, three-component synthesis of a N-alkylated amide from benzaldehyde (**7**), hydroxylamine hydrochloride, and benzyl alcohol (**2a**) through a tandem condensation/rearrangement/*N*-alkylation process was examined. As shown in Scheme 4, the desired product (**4aa**) was obtained in 81% yield.

Notably, apart from the desired N-alkylated amides, no intermediate amides or over-alkylated N,N-dialkylated amides were obtained as by-products in all cases.

In summary, we have demonstrated a new and simple strategy for the direct synthesis of N-alkylated amides from aldoximes and alcohols through a tandem rearrangement/N-alkylation process by using a Ru/Ir dual-catalyst system. Notably, this environmentally friendly reaction exhibited various advantages, such as readily available starting materials, excellent selectivities for the N-alkylated amides, and high atom efficiency. Further studies to expand the synthetic application of this strategy and to explore the potential of alcohols in tandem reactions are currently underway.



Scheme 3. Reaction of aldoximes **1a**, **1g**, and **1i** with diol **5**.



Scheme 4. One-pot, three-component synthesis of N-alkylated amide.

Experimental Section

General procedure for the synthesis of N-alkylated amines from aldoximes and alcohols

To an oven-dried, nitrogen-purged Schlenk tube (25 mL) were added [{Ru(*p*-cymene)Cl_2}$_2$] (0.005 mmol, 0.5 mol%), [(Cp*$IrCl_2$)$_2$] (0.005 mmol, 0.5 mol%), the aldoxime (1 mmol), and toluene (1 mL) and the mixture was heated at 130 °C for 3 h. Then, the reaction mixture was allowed to cool to

ambient temperature and the alcohol (1.2 mmol) and Cs_2CO_3 (0.2 mmol, 0.2 equiv) were added. The Schlenk tube was flushed with nitrogen gas and the mixture was heated at 130 °C for a further 12 h. Then, the reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography on silica gel (hexanes/EtOAc) to afford the product.

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Keywords: alcohols · alkylation · iridium · rearrangement · ruthenium

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[24] No reaction took place in the presence of a metal complex or a base alone, thus indicating that the combination of a metal source and a base is necessary for the N-alkylation reaction.

[25] The decomposition of benzaldoxime can occur in the presence of base under heating; thus, the rearrangement and N-alkylation reactions with alcohols proceed step by step.

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